Message

From: Leung, Lam-Wing H [LAM.H.LEUNG-1@chemours.com]
Sent: 11/12/2020 4:21:28 PM
To: Strynar, Mark [Strynar.Mark@epa.gov]
CC: Risen, Amy J [amy.risen@ncdenr.gov]; Delinsky, Amy [amy.delinsky@ncdenr.gov]
Subject: RE: ?RE: ?isomers of PMPA and PEPA and initial efforts

Hi Mark,

Thanks for the message and the detailed info you provided and I am also delighted to learn that we are in agreement with the "unique" MRMs for both PMPA (229-->185) and PEPA (279→235). As for your observation of the 10% "linear PMPA" in the well samples, I have the following comments:

1. Based on our limited experiments (see results box I provided earlier and below for the PMPA only standard), PMPA does show a positive response for the 229→85 MRM and at 1ppb, it represents around 15% so it's probably worthwhile to double check this ration at different concentrations. I also appreciate your observation that the retention time of these peak can be shifting as they elute so early.

MRM transitions	Peak Area				
	PEPA 1PPB Standard	PMPA 1PPB Standard	PFECA A 1PPB Standard	PFECA F 1PPB Standard	Mixed 1PPB Standard
279→234.9	1314.47	No peak	No peak	No peak	1181.01
279→85	No peak	No peak	3381.46	No peak	3495.68
229→184.9	No peak	1494.66	No peak	No peak	1347.27
229→85	No peak	218.6	No peak	3248.8	2987.24

2. Furthermore, can you please provide us with the history of the well samples (specifically when they were collected) such that we can check the exact concentration of PMPA and PEPA concentrations reported for these samples and we can then potentially estimate the "% contribution" of the "linear MRM" based on the PMPA concentration.

Thanks again for the detailed information you provided.

Best Regards,
Lam

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From: Strynar, Mark <Strynar.Mark@epa.gov>
Sent: Tuesday, November 10, 2020 12:04 PM
To: Leung, Lam-Wing H <LAM.H.LEUNG-1@chemours.com>
Cc: Risen, Amy J <amy.risen@ncdenr.gov>; Delinsky, Amy <amy.delinsky@ncdenr.gov>
Subject: ?RE: ?isomers of PMPA and PEPA and initial efforts

Lam,

I have made further progress and can get chromatographic separations here are a few slides I am working on for NCDEQ. (see slide 2 for chromatographic separation). I think we are in agreement based on your text below with some modifications.

I have done work on my QTOF and on my LC-MS/MS system. PFECA-A and PFECA-F DON'T lose a CO2 as the PMPA and PEPA does easily, so these can be used as unique transitions for PMPA and PEPA.

1. PMPA transitions (after source CO2 loss) are all unique for 185-119; 185-85; 185-69 (see slide 3)
2. The transition for PFECA-F 229-85 is not unique (see slide 3) but I can get two peaks with the latter being PFECA-F.
3. PEPA transitions (after CO2 loss) 235-135; 235-119 and 235-69 are all unique (see slide 4).
4. The transition for PFECA-A is unique for 279-85 (see slide 4)

I do see evidence of the liner version of PMPA (PFECA-F) as about 10% of the PMPA peak and a couple of the selected well samples LTW-04 and SMW-06B (see slides 5 and 6) I shown here. All so far show evidence of this peak at about 10% of the PMPA peak. I am working on some integrations to share. The RT of the early eluters are really prone to some movement so the RT do drift about a bit.

For the linear versions of PEPA (PFECA-A) in the real well samples for 279-85 I see two peaks but they are very low responders (no slide shown) an neither co-align with PEPA???

Mark

From: Leung, Lam-Wing H <LAM.H.LEUNG-1@chemours.com>
Sent: Tuesday, November 10, 2020 10:42 AM
To: Strynar, Mark <Strynar.Mark@epa.gov>
Subject: RE: ?isomers of PMPA and PEPA and initial efforts

Hi Mark,

Thanks for your message and I apologize for the late response on this. As I mentioned previously, your "initial finding" is consistent with what we observed. I have listed below results from our experiments using our "Table 3" method for 1ppb standard in water (the mixed standard contains 1ppb of each individual analyte). As you can see, we might not be able to separate them chromatographically, we can successfully separate them spectrally. We are in the process of running the same standards with Method 533 as it uses somewhat different conditions and I'll keep you posted on this. I do like to know if you have made any more progress on this recently and perhaps we can discuss further later this week or sometime next week. We have communicated these limited findings to DEQ and I am hoping that we will be able to "settle" this soon. Thanks again.

MRM transitions	Peak Area				
	PEPA 1PPB Standard	PMPA 1PPB Standard	PFECA A 1PPB Standard	PFECA F 1PPB Standard	Mixed 1PPB Standard
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Best regards,
Lam

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From: Strynar, Mark <Strynar.Mark@epa.gov>
Sent: Monday, October 26, 2020 10:09 AM
To: Leung, Lam-Wing H <LAM.H.LEUNG-1@chemours.com>
Subject: ?isomers of PMPA and PEPA and initial efforts

Hi Lam,

I have done some initial work on my QTOF for looking at PMPA vs PFECA-F (aka PFMOPrA) and for PEPA vs. PFECA-A (aka PFMOBA).

I still need to do work on my QQQ, however on the QTOF here are my initial findings and I wanted to see if they support what you are seeing. I ran each compound in MS mode only then I ran MS/MS at 10, 20 and 40 volts looking at the precursor ion for each M-H, and the CO2 loss mass. All of these were prepared an run at approximately the same concentrations. The PEPA and PMPA came from the 0.1% in water solutions you gave to me some time back. The PFECA-A and PFECA-F came from neat preparations I made up last week.

1. PMPA (m/z 228.9) readily decarboxylates in the gas phase of the source to give the ion (m/z 184.9). The ratio of the M-CO2 to the M-H is about 10:1 in the source alone.

2. PEPA (m/z 278.9) likewise readily decarboxylates like PMPA to give the ion (m/z 234.9). The ratio is similar at 10:1 for the M-CO2 to the M-H is about 10:1 also.
3. The insource loss of the CO2 is consistent with what I see with the HFPO-DA (m/z 328.9) and the corresponding fragment (m/z 284.9) so this makes sense I see this for PMPA and PEPA.
4. PFECA-F and PFECA-A really don't seem to lose the CO2 readily in the source or in MS/MS mode. The M-CO2 peak for both is really non-existent. When I isolate either and change fragmentor voltage's the main ion is the CF3O (m/z 84.9) for both. I will have to look for any other fragments more closely.

I will have more later but these are my first impressions.

Mark

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